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Chemical Communications

COMMUNICATION

Cp*Co(IPr): Synthesis and Reactivity of an Unsaturated Co(I) Complex

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Synthesis of coordinatively unsaturated Cp*Co(IPr) (2), is accomplished by addition of free N-heterocyclic carbene IPr to [(Cp*Co)$_2$-μ-(η^4:η^4-toluene)] (1). Stoichiometric reactivity is consistent with a 16 electron species, as 2 undergoes ligand addition/NHC displacement and reversible reaction with dihydrogen. Cp*Co(IPr) represents an elusive example of a stable Cp*CoL fragment.

Low valent metals are often utilized to break an array of bonds in small molecules, allowing for further elaboration to a range of value added products. Such strategies have proven effective for both the stoichiometric and catalytic functionalisation of carbon dioxide,[1] dinitrogen,[2] and hydrocarbons.[3] In particular, Ir mediated alkane dehydrogenation has permitted access to a variety of potentially useful transformations,[4] including dehydroaromatisation to produce substituted benzenes[5] and tandem catalysed alkane metathesis.[6] Although such Rh and Ir catalysed C-H activations with a range of substrates are now well established,[7-10] preparation of analogous Co complexes capable of performing similar chemistry has lagged. Recent work provides promise in the area, as examples of intramolecular sp^2 and sp^3 C-H activations with cobalt are now well established.[11,12] Catalytic sp^2 C-H activation and functionalisation of aromatic substrates is also an expanding field.[13] Moreover, reports of cationic Cp*Co(III) mediated catalysis involving sp^2 C-H and C-C bond activation and functionalisation have recently appeared.[14,15]

The difficult task of activating alkane C-H bonds with first row metals is likely a result of a combination of factors, involving both the propensity for these metals to participate in one electron redox processes and spin state issues not typically encountered with second and third row congeners. Classic studies by Bergman and coworkers illustrate these subtle dynamics and demonstrate that access to unsaturated low valent metals is not the only prerequisite for C-H activation.[16] For example, in the series of Cp*ML (M = Co, Rh, and Ir, L = CO) species, generated at 173 K in liquid Kr matrices, the Rh and Ir intermediates readily react with aliphatic C-H bonds while the corresponding Co version undergoes secondary reactivity rather than binding and cleaving carbon-hydrogen bonds. Computational studies suggest this difference in reactivity is caused by the predicted triplet nature of the Co intermediate, resulting in a high barrier to spin crossover which prevents productive reaction with a singlet C-H bond.[17,18] Since these seminal studies, others have encountered similar issues while accessing unsaturated Co(I) species, with lack of reactivity with carbon-hydrogen bonds again being attributed to the triplet nature of the complex.[19]

Our groups initial interest in Cp*CoL fragments stemmed from attempts to generate the Cp*Co(η^2-fumarate) fragment, as a related species was noted as a key intermediate engendering air and water stability to Co catalysed [2+2+2] cycloaddition reaction of alkynes.[20] Upon addition of dimethyl fumarate to [(Cp*Co)$_2$-μ-(η^4:η^4-toluene)] (1),[21] sp^2 C-H activation of the fumarate was observed to form a bridging dicobalt hydride complex.[22] As the potential mechanism implied access to a 16 electron fragment prior to C-H activation, this suggested further investigation of analogues of the Bergman system were in order. Such study could permit the observation or isolation of a Cp*CoL fragment, providing a deeper understanding of the nature of the electronic structure and small molecule reactivity of these species.

Here we report the isolation, characterisation, and reactivity of such a Cp*CoL complex, where L is the N-heterocyclic carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr).[23,24] Cp*Co(IPr) (2) has been characterised by numerous methods, including X-ray crystallography and mass spectrometry. Computational studies further support the observed triplet ground state of the molecule. Reactivity of 2 is consistent with an unsaturated Co(I) species, as the complex undergoes ligand addition/carbene displacement as well as reversible reaction with dihydrogen. Complex 2 provides a robust entry point into the chemistry of Cp*CoL fragments, in stark contrast to the fleeting nature of Cp*Co(CO).

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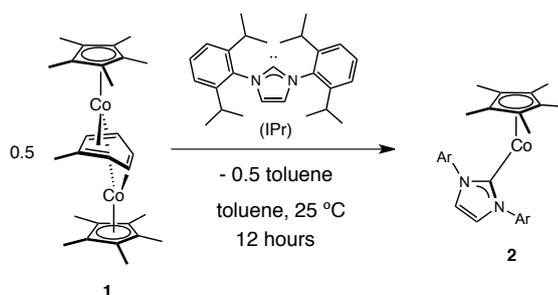   Email: cbradley@msmary.edu; Phone: 301 447 5285; Fax: 301 447 5021.
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Scheme 1 Synthesis of Cp*Co(IPr) (**2**).

Stirring **1** with N-heterocyclic carbene ligand IPr in aromatic solvent results in evolution of toluene and formation of the desired 16 electron Cp*Co(IPr) complex **2** (Scheme 1). Monitoring the reaction by ^{1}H NMR spectroscopy in benzene-d_6 reveals that only **2** is formed even in the presence of excess IPr, likely a result of the steric demands of the NHC ligand. Complex **2** displays a broadened paramagnetic ^{1}H NMR spectrum with wider peak dispersion (~30 ppm) than diamagnetic molecules. This is further corroborated by solution magnetic susceptibility studies (Evans method) performed in benzene-d_6,[25] with a μ_{eff} = 2.6(1) μ_B for **2** at 25 °C. Though this μ_{eff} value is lower than expected for two unpaired electrons, a related bis(indenyl) cobaltate anion gave similar measurements.[26] LIFDI mass spectrometry[27] further establishes the composition of **2**, with a parent ion observed at m/z = 582.

X-ray quality crystals of **2** were grown from an ether:pentane mixture at −30 °C and supports the formation of Cp*Co(IPr) (Figure 1). Pertinent Co-Cp* metrics in the molecule are within ranges observed in other known Cp*Co(I) complexes.[28-30] The Co-C$_{IPr}$ distances of 1.943(2) and 1.946(2) Å are slightly elongated relative to comparable bonds found in the related Cp*Co(^{i}Pr$_2$Im)(η^2-ethylene) complex.[31] Of note, the Cp*(centroid)-Co-C$_{IPr}$ angle deviates from linearity, by 18° and 20°, in the two molecules in the asymmetric unit. This bent ground state structure is consistent with calculations performed on **2** (*vide infra*). Furthermore, **2** is structurally similar to the Cp*Ni(IPr) analogue recently prepared,[32] suggesting the bent structure is an energetic minimum balancing the steric congestion imparted by the Cp* and IPr ligands.

A geometry optimisation was performed on **2**, using the coordinates determined from the X-ray structure study. Both singlet and triplet states were computed. In addition, a "linear" version of **2** (with an optimised Cp*(centroid)-Co-C$_{IPr}$ angle of 174°) was also geometry optimised for both the singlet and triplet states. The energies of these structures were calculated using the OLYP functional, to avoid overestimation of triplet energetics.[33,34] Experimental and calculated metrics for the bent geometry are in reasonable agreement, with a calculated Cp*(centroid)Co-C$_{IPr}$ angle of 159° in the bent triplet. Energetically, there is a strong preference for the triplet state in each geometry, with singlet-triplet gaps of >14 kcal/mol in both cases. Comparing the triplet states of each geometry, the bent triplet, experimentally observed, has a slightly lower energy than the corresponding linear triplet. Examining the population analysis of the four structures indicates there is some degree of back donation from ligand to metal, as the α HOMO-11 orbital is composed of 19% C(carbene) and 17% Co d orbital for the bent triplet structure. The other calculated structures also displayed similar parentages for this orbital.
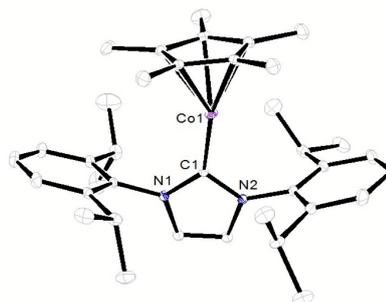

Figure 1. Molecular structure of **2** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity (1 of 2 molecules in the asymmetric unit shown). Selected bond distances/ranges (in Å): Co-Cp* distances: 2.09-2.17, Co-C$_{IPr}$ distances: 1.943(2)/1.946(2).

The small molecule reactivity of **2** is further consistent with a 16 electron complex. Addition of excess carbon monoxide to **2** results in immediate reaction, as monitored by ^{1}H NMR spectroscopy, to provide the mixed ligand complex Cp*Co(IPr)(CO) (**3**) (Scheme 2). Complex **3**, as expected for an 18 electron complex, is diamagnetic, displaying a bound CO resonance at 220.48 ppm in the ^{13}C NMR spectrum recorded in benzene-d_6. The carbonyl is terminal, based on the observed CO stretch at 1884 cm^{-1} in the IR spectrum recorded in pentane, in accord with the carbonyl stretches seen in Cp^{Rn}Co(^{i}Pr$_2$Im)(CO).[35,36] Further establishment of the structure of **3** was provided by an X-ray structure determination, performed on crystals grown from ether:pentane at -30 °C (Figure 2). Compound metrics are within standard ranges for known IPr and Cp*Co(I) complexes.[11,28-30] Of particular interest is the angle formed between Co-C$_{IPr}$- NHC$_{centroid}$ of 167°. This differs significantly from **2** and Cp*Co(^{i}Pr$_2$Im)(CO)[31] which have analogous angles of 175° and 180°, respectively. The observed canting of the NHC core in **3** is likely necessary to accommodate the additional carbonyl ligand. If such significant geometric distortion is required to bind two ligands, this may help explain substitution chemistry observed with other more sterically encumbering small molecules (*vide infra*).

	Bent Geometry	Linear Geometry
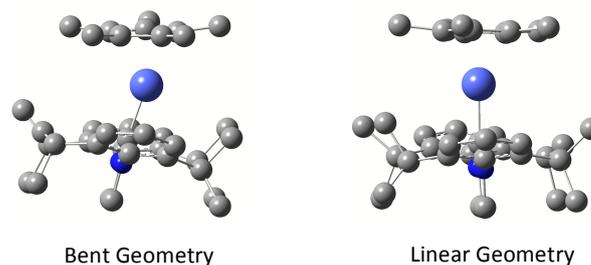
Calculated geometry/ spin state of 2	Calculated Energy (atomic units, au)	Relative Energy (kcal/mol)
Bent(singlet)	-1694.81465710	14.3
Bent(triplet)	-16954.83750623	0.0
Linear(singlet)	-1694.80562651	20.0
Linear(triplet)	-1694.83418903	2.1

Table 1. Optimised structures (for triplet states only) and calculated total energies for **2**. Computational details: Gaussian 09, OLYP exchange/correlation functional with LANL2TZ+F on Co and 6-31g(d',p') on all other atoms.
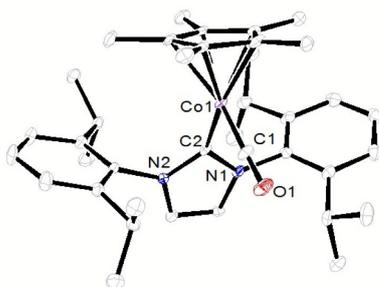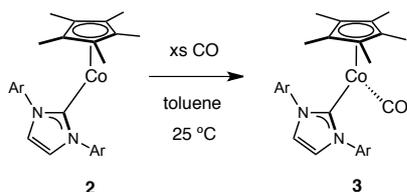
Figure 2. Molecular structure of **3** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances/ranges (in Å): Co-Cp* distances: 2.05-2.12, Co-C(2) distance: 1.902(5), Co-C(1) distance: 1.695(4), C(1)-O(1) distance: 1.171(5). Selected bond angles (in °): C(1)-Co-C(2) angle: 88.93, Co-C(1)-O(1) angle: 177.44.


Scheme 2. Addition of carbon monoxide to **2**.

Reactivity differences are observed when **2** is exposed to other σ and π donors (Scheme 3). Weaker σ donors, such as 4-dimethylaminopyridine (DMAP), do not react even with heating. However, addition of excess trimethylphosphine results in reaction at 65 °C to provide Cp*Co(PMe$_3$)$_2$ (**4**) and free IPr. This is confirmed by ^{1}H and ^{13}C NMR spectroscopy, and LIFDI mass spectrometry of the reaction mixture when compared to authentic samples of independently prepared **4** and IPr (ESI, Figure S12). Similar carbene displacement is observed, under ambient conditions, upon exposure of **2** to excess ethylene, generating IPr and Cp*Co(η^2-H$_2$C=CH$_2$)$_2$ (**5**), which can again be confirmed by comparison to the spectroscopy of the known compounds. The observed substitution of a strong σ donor may result from the steric pressure imparted in the potential mixed ligand Cp*Co(IPr)L complexes, resulting in loss of free carbene. Interestingly, the carbene ligand in **3** is not displaced, even in the presence of excess CO at ambient temperature. This dramatic difference in carbene displacement with various L donors is under further investigation in our laboratory.

Besides ligand addition and substitution chemistry, a 16 electron Cp*Co(I) complex would be expected to participate in oxidative addition chemistry, as observed recently in stoichiometric reactivity of PNP Co pincer systems.[37] Exposure of **2** to four atm of dihydrogen results in immediate reaction to provide a diamagnetic product we currently identify as the compressed dihydride Cp*Co(IPr)H$_2$ (**2-^{c}H$_2$**) (Scheme 4), a result of oxidative addition of dihydrogen. In particular, an upfield shifted resonance, integrating to two hydrogens per molecule, is observed at -17.78 ppm in the ^{1}H NMR spectrum recorded in benzene-d_6. The peak is absent when **2-^{c}D$_2$** is prepared upon addition of D$_2$ to **2**.
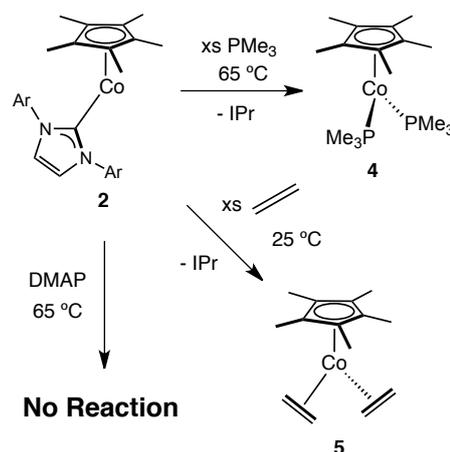
**Scheme 3.** Reactivity of **2** with σ and π type donors.
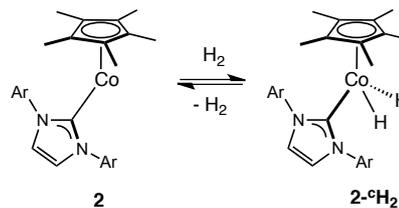
Scheme 4. Reversible reaction of dihydrogen with **2**.

In our hands, it has proven difficult to isolate and fully characterise **2-^{c}H$_2$**. Complete removal of the hydrogen gas and solvent results in immediate regeneration of **2**. Efforts to freeze the solution, remove the hydrogen atmosphere in the headspace, and crystalize **2-^{c}H$_2$** has resulted only in isolation of **2**. Attempts to identify Co-H/Co-D stretches by IR spectroscopy in **2-^{c}H$_2$** and **2-^{c}D$_2$** have also proven unsuccessful. To further distinguish between a dihydride and dihydrogen complex, **2** was exposed to H-D gas in an attempt to measure the H-D coupling constant of the isotopologue. Due to the broadness of the resonance (~ 40 Hz), the coupling in **2-^{c}(HD)** could not be definitively measured, even at low temperature. Fortunately, a T$_1$(min) value of 91 ms, corresponding to an H-H distance of 1.38 Å, was recorded for the hydride resonance of **2-^{c}H$_2$** at 245 K, indicative of a compressed hydride.[36]

Geometry optimisations were performed for singlet dihydride, singlet/triplet compressed dihydride (where the H-H distance was locked at 1.38 Å), and singlet/triplet dihydrogen complex. The lowest energy minima located were a singlet state cobalt(III) dihydride complex and the singlet compressed dihydride (Table 2, ESI). These two structures were of comparable energy (within 2.5 kcal/mol of one another) and much closer in energy than the corresponding triplet structures, which lie more than 10 kcal/mol above the singlet states. These results are suggestive of the significant dihydride character of **2-^{c}H$_2$** while highlighting the need for experimental data to accurately assign structure.

Thermolysis experiments with **2** were also performed in aromatic solvents. Unfortunately, no thermal activation of C-H bonds has been observed to date. Heating toluene solutions of **2** at 100 °C for a week results in no discernible change, based on ^{1}H NMR spectroscopy. This result is consistent with the large calculated singlet-triplet gap (*vide supra*) and further illustrates how issues of spin continue to plague efforts to activate aliphatic C-H bonds with cobalt. Given the remarkable stability of **2**, we are currently

2-H₂
(singlet)

2-(η²-H₂)
(triplet)
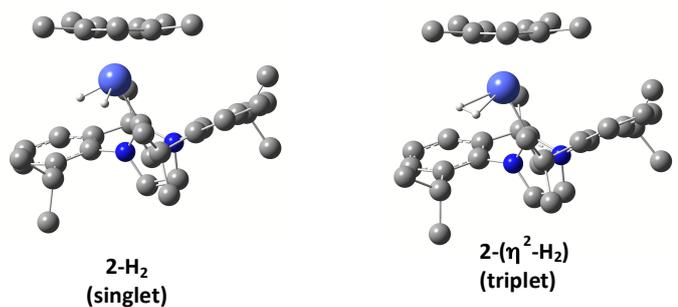
Complex	Calculated Energy (atomic units, au)	Relative Energy (kcal/mol)
2-H₂ (singlet)	-1696.01843440	0.00
2-ᶜH₂ (singlet)ᵃ	-1696.01442988	2.50
2-ᶜH₂ (triplet)ᵃ	-1695.99297040	16.00
2-(η²-H₂) (triplet)ᵇ	-1695.97685341	26.10

ᵃThe H-H distance was frozen at 1.38 Å. ᵇ A singlet energy minimum for the dihydrogen complex could not be located.

Table 2. Optimised structures (for two of the complexes) and calculated total energies for Cp*Co(IPr)H₂, compressed Cp*Co(IPr)H₂ and Cp*Co(IPr)(η²-H₂). Computational details: Gaussian 09, OLYP exchange/correlation functionals with LANL2TZ+F on Co and 6-31g(d',p') on all other atoms.

exploring more forcing thermal and photolytic conditions in an effort to observe intra- or intermolecular oxidative addition of carbon–hydrogen bonds.

In summary, we have demonstrated synthesis of an elusive Cp*CoL fragment. Complex **2** displays the rich chemistry expected of an unsaturated Cp^{Rn}Co(I) center,[40] participating in ligand addition as well as two electron oxidative processes. Though **2** to date is unreactive with alkanes, we plan to continue to study the stoichiometric activation of other E-H bonds with the molecule, as well as exploring the use of **2** as a precatalyst in transformations involving activated alkene containing substrates, given the lability of the IPr fragment under mild conditions in the presence of ethylene.

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